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MATHEMATICAL MODELING OF ADHESION OF ENAMEL TO STEEL

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Undercoat enamels for steel with increased strength of adhesion are synthesized on the basis of alumina-bearing waste. Mathematical modeling is implemented and a regression equation is obtained.

One of the most difficult problems in synthesis of protective glass enamel coatings for metals is the development of strong adhesion of coating to the substrate. It is traditionally believed that the main condition is to select the TCLE of the enamel to be 10 – 15% lower than the TCLE of the substrate. However, some coatings are known to have stable adhesion to metal despite the fact that this condition is not satisfied [1]. On the contrary, in the synthesis of coatings for certain metals, for instance for aluminum, we were confronted with the fact that even when the TCLEs of the coating and the metal correlated, defects in the form of chips were observed in the coating.

Another generally accepted condition for strong adhesion is the presence of adhesive oxides in the composition, such as cobalt and nickel oxides. However, the practice shows that oxides of other metals as well can participate in adhesion, such as chromium, iron, and molybdenum, whose mechanism is not fully studied. There are also some known compositions of single-layer coatings that do not contain the above listed oxides, but have sufficient strength of adhesion to the substrate (RF patent No. 2141458) [1].

Consequently, the adhesion of coating to the substrate is a complex physicochemical process depending on a combination of factors (Scheme 1).

The purpose of our study is to identify the effect of the quantity and type of modifiers and glass-forming agents on the expansion of the firing temperature interval and the strength of adhesion of undercoat enamels on steel.

The advantage of the synthesized prime coatings is that costly alumina in their composition is replaced by alumina-

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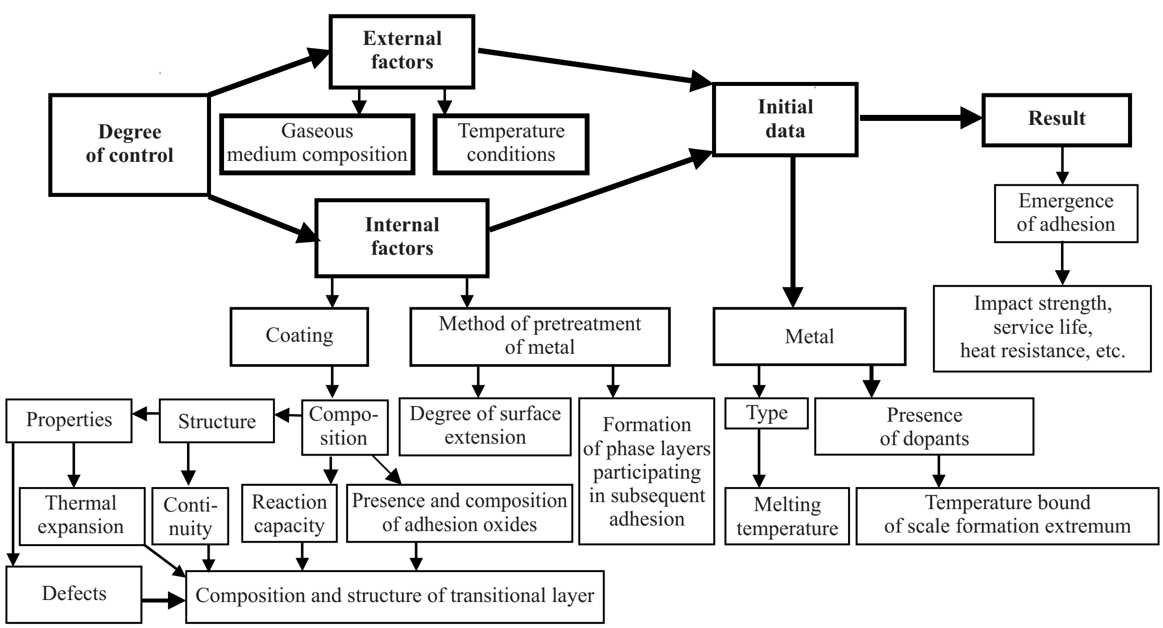

Scheme 1. Structural-logical scheme of adhesion formation in the metal – single-layer glass-composite coating system in heat treatment.

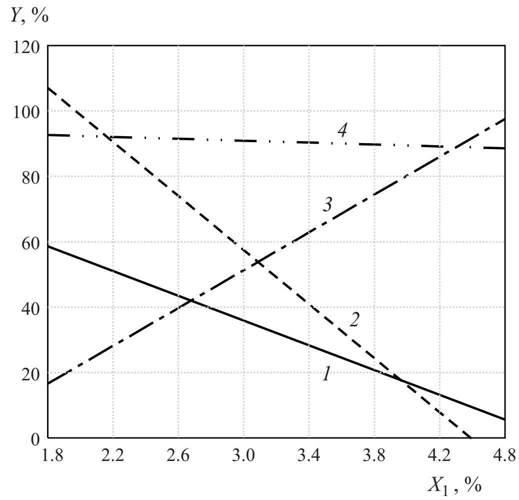

Fig. 1. The effect of variable X_1 on the response function Y: *1*, *2*, *3*, and *4*) X_2 = 16, 18, 20, and 22%, respectively.

bearing waste from the Belokalitvenskii Metallurgical Works. The problems of using industrial waste in production is topical now, since in some sectors of industry the volume of generated waste exceeds hundreds of thousands of times the yield of the target product. At present about 2 – 3 billion technological products are being regularly produced and as many byproducts. Totally safe waste does not exist. Thus, a hectare of dumping grounds for slag contaminates at least 5 hectares of adjacent land. The dumping sites in our country annually emit into the atmosphere 42 millions m^3 of sulfur dioxide, 4 millions m^3 of carbon dioxide, and 2 millions m^3 of hydrogen sulfide [2]. The main requirements imposed on using such waste include its environmental and radiation safety. The waste from the Belokalitvenskii Metallurgical Works, besides its radiation and bacteriological safety, has a sufficiently high content of the main component, i.e., Al_2O_3 (72.3%); therefore, it has been successfully applied in compositions for undercoat enamels for steel of grades 0.8kp and st.3 [3, 4].

The variation factors (independent variables) were selected in accordance with the specified task; their values are given in Table 1.

Bounds and increments for each independent variable were selected sufficiently wide to account for the maximum degree of all possible variants. The dependent variable (the response function) was the strength of adhesion of coating to steel 08kp determined according to the method developed at the modeling laboratory of the NPI Institute [5].

The originality of this experiment consisted in the fact that the object of study was not the effect of the content of adhesive oxides, but the effect of the qualitative and quantitative composition of the glass matrix on the strength of adhesion for a constant weight content (%): 1.5 Fe_2O_3, 0.5 CoO, 1.5 NiO, 1.0 MnO_2, 1.0 TiO_2. 5.5 waste, and 7.0 – 13.0 CaO depending on the content ($Na_2O + K_2O$). The type of

TABLE 1

Designations of independent variable	Name of variable	Variation limits	Interval
X_1	Ratio $SiO_2 : B_2O_3$ at ($SiO_2 + B_2O_3$) = 60 wt.%	2.0 – 4.2	0.6
X_2	Weight content of ($Na_2O + K_2O$) with ratio $Na_2O : K_2O$ = 1.1 : 1.0 wt.%	16 – 22	2
X_3	Firing temperature, °C	760 – 920	40

TABLE 2

Variation factors		Response function Y (adhesion strength), % at X_3, °C				
X_1	X_2	760	800	840	880	920
2.0	16	0	80	70	50	98
	18	85	99	99	98	97
	20	0	0	0	0	20
	22	0	97	95	95	97
2.6	16	0	10	10	10	10
	18	90	99	95	99	95
	20	0	0	50	50	50
	22	0	95	95	95	97
3.2	16	0	0	20	20	70
	18	0	0	10	20	10
	20	20	97	93	93	93
	22	0	0	80	97	97
3.8	16	0	0	10	10	10
	18	0	0	30	30	30
	20	0	0	30	30	30
	22	10	99	92	93	95
4.2	16	0	0	30	30	30
	18	0	0	20	20	40
	20	0	80	80	50	50
	22	1	95	93	90	95

the planning matrix combined with the experimental results is reflected in Table 2.

Based on the experimental results, plots of pairwise dependences of the response functions were constructed for each variable (Fig. 1). Of special interest are the dependences for several groups of data with different X_2 and varying values of X_1 . The temperature of 840°C is the optimum for energy saving, since adhesion at lower temperatures has low absolute values and is unstable.

It can be seen that with growing X_1, the values of Y decrease, provided that $X_2 < 20$; at $X_2 = 20$ the values of Y increase; and at $X_2 > 20$, the values of Y stabilize with increasing X_1 . An analysis of the similar pairwise dependence of Y on X_2 at X_3 = 840°C indicated that with increasing total content of the alkali components, the adhesion strength keeps increasing within the whole variation interval.

Evidently it is necessary to identify the optimum and the limiting content of the alkali components taking into account the chemical resistance of the coating and the temperature interval of firing.

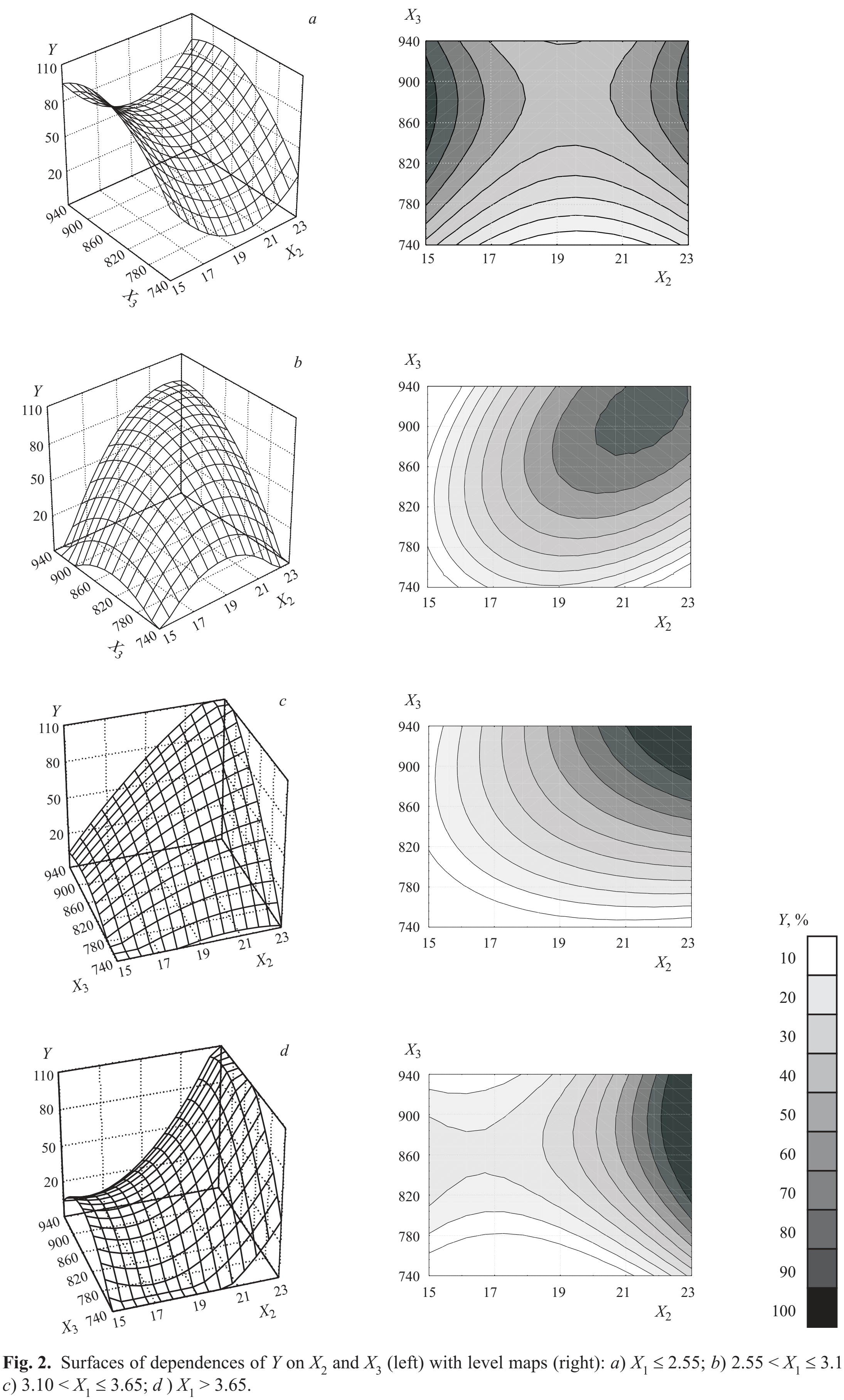

Fig. 2. Surfaces of dependences of Y on X_2 and X_3 (left) with level maps (right): *a*) $X_1 \leq 2.55$; *b*) $2.55 < X_1 \leq 3.10$; *c*) $3.10 < X_1 \leq 3.65$; *d*) $X_1 > 3.65$.

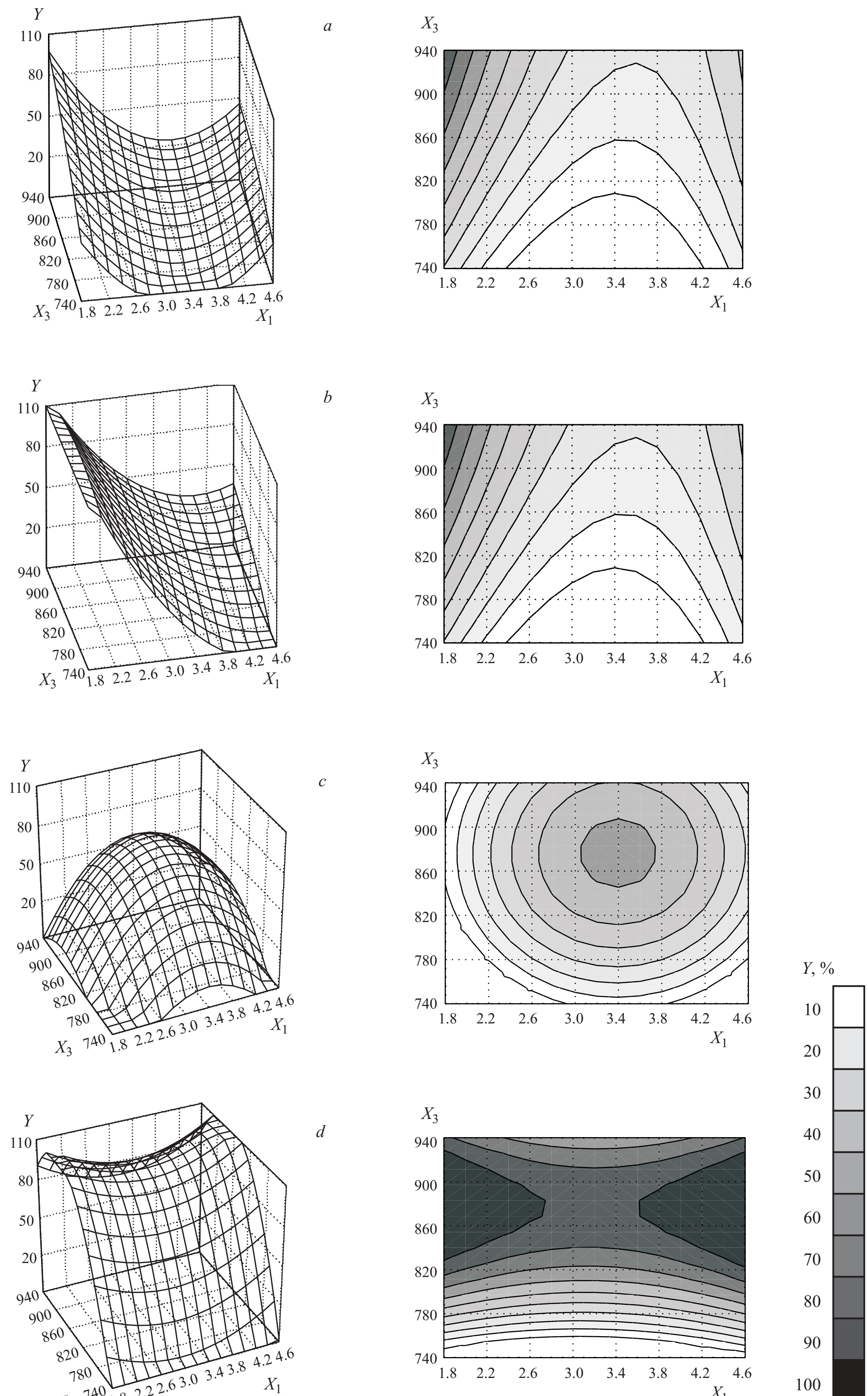

Fig. 3. Surfaces of dependences of Y on X_1 and X_3 (left) with level maps (right): *a*) $X_2 \leq 17.5$; *b*) $17.5 < X_2 \leq 19.5$; *c*) $19.5 < X_2 \leq 20.5$; *d*) $X_2 > 20.5$.

After processing of experimental results, a mathematical model (regression equation) was obtained:

$$Y = -287.172 - 11.175X_1 + 6.91X_2 + 0.281X_3 .$$

The determination coefficient of the equation is equal to 0.32, i.e., the variability of values of the variable Y near the regression line is 0.68 of the initial dispersion; in other words, it can account for up to 32% of the initial variability [4]. Since the lower temperature bound in the experiments was shifted to a relatively low-temperature range for this technological process, it is evident that elimination of this temperature segment will increase the determination coefficient and, consequently, the values obtained from the regression equation. It is also necessary to note that, judging from the signs before the coefficients in the equation, the relationship of Y to X_1 is negative and the relationship of Y to X_2 and Y to X_3 is positive. Furthermore, all coefficients in the equation are significant.

For the purpose of quantitative description of differences between the observed groups, modeling of surfaces was carried out (the plots of the latter were obtained by quadratic smoothing) for different grouped variables, and the level line maps were constructed, which represent projections of three-dimensional surfaces on a two-dimensional plane (Figs. 2 and 3). The equations describing these surfaces have the following form:

$$Y = -1099.04 - 99375X_2 + 4.784X_3 + 2.3(X_2)^2 + 0.012X_2X_3 - 0.003(X_3)^2 \quad \text{for } X_1 \leq 2.55;$$

$$Y = -2020.444 + 35.32X_2 + 3.799X_3 - 2.575(X_2)^2 + 0.083X_2X_3 - 0.003(X_3)^2 \quad \text{for } X_1 = 2.55 \text{ and } 3.10;$$

$$Y = -895.731 - 18.795X_2 + 2.089X_3 - 0.65(X_2)^2 + 0.062X_2X_3 - 0.002(X_3)^2 \quad \text{for } X_1 = 3.10 \text{ and } 3.65;$$

$$Y = -1333.275 - 109.845X_2 + 5.248X_3 + 2.269(X_2)^2 + 0.041X_2X_3 - 0.003(X_3)^2 \quad \text{for } X_1 > 3.65.$$

Similar equations were obtained for the dependences of Y on X_2 and X_3. The modeling was implemented using the Statistika software package [6].

An analysis of the plots of three-dimensional surfaces revealed the following. With $X_1 < 2.5$, the adhesion strength values close to the optimum correlate with the ($Na_2O + K_2O$) content up to 16% and more than 20%. With X_1 increasing to over 2.55, the range of the optimum values shifts to an alkali content over 20% (Fig. 2*b* and *d*).

In varying the $SiO_2 : B_2O_3$ ratio, the largest area under certain dynamic states of the total content of alkalis is taken by the optimum range with the content of ($Na_2O + K_2O$) > 20.5% (Fig. 2*d*). In this case the firing temperature interval of the coating decreases to 840 – 880°C, which is the optimum value.

Thus, the application of the mathematical modeling methods in addition to complete factor planning and mathematical processing of experimental data makes it possible to represent most visibly the results and to identify further research problems.

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